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Evidence for surface initiated solidification in Ge films upon picosecond laser pulse irradiation

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Amorphous Ge films on Si films have been melted by single 30 ps laser pulses at $\lambda = 583$ nm and a solidification process has been followed by means of real time reflectivity (RTR) measurements with nanosecond time resolution. Evidence is provided for the occurrence of surface initiated solidification for films with thicknesses in the 80–130 nm range. This process occurs at high fluences following complete melting of the film and of a thin layer of the Si substrate which undergoes mixing with the liquid Ge. The release of the solidification enthalpy of the latter layer together with its lower solidification temperature favored by constitutional undercooling are proposed as the origin of the initial gradient inversion required for such a process. This scenario leads also to the formation of a secondary solidification front counterpropagating towards the film surface, as suggested by optical simulations of the experimental RTR transients. A transition from a surface initiated solidification process towards a bulk solidification process is shown to occur when increasing the film thickness beyond 130 nm. The results further show that, besides the film thickness, the pulse duration has a major influence on the type of solidification process induced. [DOI: 10.1063/1.1347958]

I. INTRODUCTION

Considerable effort has been spent since the mid-1970s on the study of the different solidification scenarios taking place in semiconductors upon pulsed laser melting.[1] Initially, it was motivated by interest in the properties of liquid and solid phases of a material far from the thermal equilibrium[2,3] and in the application of laser annealing to recover damage induced by ion implantation in semiconductors.[1,4] Nowadays, this subject still receives much attention due to the wide field of applications that has become accessible during the last decades, such as pulsed laser crystallization of thin amorphous films for the fabrication of thin film transistors[5,6] and the production of materials with very specific compositions such as strained layers of narrow-band gap $Si_{1-x}Ge_x$.[7–9] Whereas most work focused on the effects of ns laser pulses, the present work attempts to contribute further to understanding of the solidification scenarios induced by subnanosecond laser pulses.

Generally, one can distinguish between two major solidification scenarios, bulk and interfacial solidification, which may even coexist under certain conditions. Bulk solidification[10–13] is characterized by the formation of solid crystalline or amorphous nuclei in a supercooled melt that is at a homogeneous temperature. This means that nuclei form all over the isothermal liquid volume and grow until they reach a critical size, above which solidification proceeds. While bulk solidification usually leads to crystallization, amorphous nuclei may be formed for very large supercoolings, leading to amorphization of the entire melted volume.[12,14]

In contrast, interfacial solidification consists of an undercooled liquid/solid interface moving towards the region of maximum temperature, which is usually located at the surface. The origin of this behavior is the nonefficient extraction of heat towards the surrounding air due to its very low thermal conductivity compared to that of a nonmolten material or substrate. Nevertheless, an interfacial solidification process that is initiated at the surface and propagates in depth has also been observed to occur in Si amorphized by ion implantation (a-Si),[15–19] although its driving force could not clearly be established. A further interfacial solidification pro-

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cess often reported is the explosive crystallization of amorphous films[20,21] during which a thin buried liquid layer propagates towards the substrate, leaving crystalline material behind. The occurrence of explosive crystallization requires an amorphous-to-crystalline transformation upon solidification because the thermodynamic driving force for the propagation of a thin buried layer into the depth is the fact that the amount of latent heat released upon crystallization is sufficiently large to melt a thin amorphous layer underneath. Both scenarios, surface initiated solidification and explosive crystallization, have in common that a solid–liquid interface propagates towards the substrate which makes it difficult to distinguish between them when probing the sample surface by optical techniques.[16,19,21–23]

In this work we demonstrate that surface initiated solidification can be induced upon ps laser pulse irradiation in amorphous Ge. We will provide experimental evidence that this solidification process occurs once the melt front reaches the Si substrate and a thin Si layer melts. The heat diffusion process occurring at the film/substrate interface together with solidification of a Si–Ge mixture are found to be responsible for the necessary transient inversion of the thermal gradient. The film thickness of the specimen has been introduced as an additional experimental parameter in order to modify the heat flow conditions in a controlled manner. We have thus been able to study the transition between three of the solidification scenarios mentioned above and to identify the heat flow conditions required by each of them.

II. EXPERIMENT AND SIMULATION

The samples used in this study were amorphous Ge films grown by dc sputtering from (99.999%) Ge targets using a vacuum system with residual pressure of 3×10^{-6} Torr and Ar operating pressure of 4×10^{-3} Torr. The deposition rate used was 0.25 nm/s, obtaining films with a thickness of 30, 50, 80, 100, 130, and 180 nm. The substrates were Si $\langle 100\rangle$ wafers covered by their native oxide and held at room temperature during deposition. The optical constants of the films were measured by a commercial spectroscopic rotating-polarizer ellipsometer. The void fraction of the films was estimated to be below 4% and relatively constant over depth for a film thickness between 50 and 200 nm.[24]

The films were irradiated by single 30 ps laser pulses at $\lambda=583$ nm focused onto the sample surface to a size of about 200 μm to reach fluences up to 320 mJ/cm^2. The absolute fluence at the sample site has been determined within 10% while determination of the relative fluence of two different pulses has an accuracy of close to 2%. In all cases, the measurements were performed by exposing areas of the film to only one laser pulse. The transient reflectivity changes induced by the ps laser pulse were monitored by a HeNe laser ($\lambda=633$ nm) focused to 50 μm onto the center of the irradiated spot. The specular reflection of this beam at the film surface was collected by a fast photodiode connected to a transient digitizer, providing a time resolution of a few ns. Further details about the detection and the laser systems used can be found elsewhere.[13,25]

Optical simulations of the induced reflectivity changes were performed using two different computer programs designed for this purpose. Both programs were tested and were shown to work successfully.[13] The first program is designed to simulate a surface initiated solidification process progressing in depth and is based on an exact mathematical description of the interaction of an electromagnetic wave with an isotropic planar multilayered system formed by layers with different refractive indexes and absorption coefficients.[26] The program transforms layer by layer the optical constants of the molten film [liquid Ge (l-Ge)][27] into the constants of the different phases involved in the solidification process [amorphous Ge (a-Ge)[24] or crystalline Ge (c-Ge)][28] and calculates the reflectivity of the whole system at the monitoring wavelength as a function of the transformation depth. The second program takes into account the case of incomplete crystallization, i.e., the conversion of the molten volume into crystallites distributed within an amorphous matrix. A good model for describing this situation is provided by effective-medium theories such as the one developed by Bruggemann[28] which is used here to calculate the reflectivity evolution of a solidifying Ge film for a given crystalline fraction. Furthermore, the possible presence of a secondary solidification front initiated at the substrate and propagating towards the surface has been taken into account. For this a fit parameter d_{sol}, i.e., the depth at which both solidification fronts meet, has been introduced. In a first approximation this can be done by taking the initial melt depth as the parameter d_{sol} in the simulation with only one solidification front propagating in depth. Since the optical penetration depth in l-Ge is very small (about 8 nm), the presence of the solidification front propagating towards the surface can hardly be detected except at a depth very close to the one at which both fronts meet. As a consequence, this approximation should be reasonable despite its simplicity.

After irradiation, the films were characterized by Raman spectroscopy in a micro-Raman configuration using a Raman spectrometer attached to a metallographic microscope for excitation and scattered light collection.[29] An argon ion laser operating at 514 nm delivered the excitation beam. In order to avoid the presence of both spectral broadening and/or annealing of the surface due to laser induced heating, the power of the excitation beam was kept low enough (a few mW) and the beam was slightly defocused, leading to spatial resolution of a few μm. Since crystalline Ge produces a strong yield at 298 cm^{-1} in the Raman spectrum compared to the relatively weak yield at 275 cm^{-1} of the amorphous material,[30] it could easily be determined whether crystallization (partial or complete) or re-amorphization had occurred upon solidification.

The concentration profiles of selected regions of the irradiated films were measured by secondary ion mass spectroscopy (SIMS). The measurements were carried out with a commercial time-of-flight secondary ion mass spectrometer of the fourth generation (TOF-SIMS-IV) using 1 keV Ar ions for sputtering and 25 keV Ga ions for analysis. Both ion sources were incident at the sample surface at an angle of 45° opposite each other. The dimensions of the sputtered area were in all cases 300 μm$\times$300 μm, whereas the dimensions of the analyzed area were 70 μm$\times$70 μm. The ejected

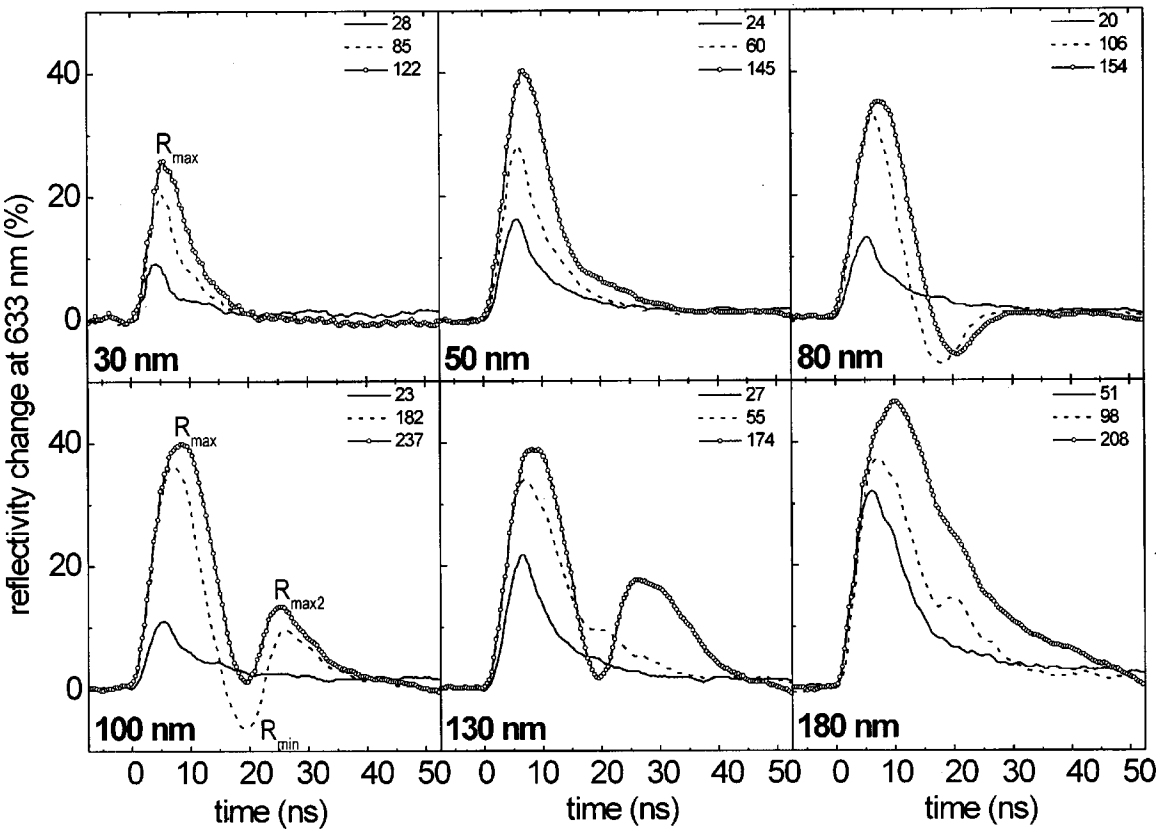

FIG. 1. Real time reflectivity transients at 633 nm in *a*-Ge films with different thicknesses on Si substrates obtained upon ps laser pulse irradiation. The laser fluences used for each transient are given in mJ/cm^2 in the legends. The characteristic reflectivity values at the maximum ($R_{\max}$), at the minimum ($R_{\min}$), and at the second maximum ($R_{\max 2}$) are indicated in the transients of the 30 and 100 nm thick films. The reflectivity changes were normalized to the reflectivity of the corresponding initial *a*-Ge film and the temporal position of the ps pulse is in all cases at $t=0$.

Ge and Si ions were detected by a 128 pixel$\times$128 pixel detector, allowing one to obtain spatial resolution of better than 1 μm by looking at individual pixels. This ensured that only the very center of each laser irradiated area contributed to the measured yield, which was important in order to allow a direct comparison to the real time reflectivity (RTR) results fulfilling the same condition. The sputter yield under the present conditions was determined (by means of the computer program SRIM2000 based on Monte Carlo simulations) to be $Y(\mathrm{Ge})=2.35$ atoms/ion and $Y(\mathrm{Si})=1.81$ atoms/ion. This means that sputtering of the Ge film is 1.24 times faster than of the Si substrate, which has been taken into account when transforming the sputter time scales into depth scales. In order to avoid matrix effects like those found in the concentration profiles at the film interface when measuring single-charged Ge and Si ions (Ge^+ and Si^+), we have measured the double-charged Si ions and the single-charged Ge dimer ions (Ge_2^+ and Si^{++}), which do not show these effects. In all cases, the intensities corresponding to all of the isotopes of the Si and Ge ions were summed up.

III. RESULTS

Figure 1 shows several representative RTR transients at different fluences for six samples with different film thicknesses. For the 30 and 50 nm thick films, a sharp reflectivity increase up to a maximum ($R_{\max}$) is observed which corresponds to film heating and melting, $R_{\max}$ being a function of the induced melt depth that is laser fluence dependent.[11,13,27] The subsequent decay of the RTR transient to the final reflectivity is related to cooling and solidification. For the 80 nm thick film, only the transients obtained at low fluences are similar to those of the 30 and 50 nm thick films, whereas for higher fluences the reflectivity maximum is followed by an oscillation below the initial level. Such a minimum, $R_{\min}$, is also observed in the transients of the 100 nm thick film but here the minimum is followed by a second reflectivity maximum, $R_{\max 2}$. For the 130 nm thick film, the behavior of the transients can be classified into three fluence regimes: At low fluences, the transients are similar to those of the 30 and 50 nm thick films. At high fluences, the transients behave similarly to those of the 100 nm thick film at high fluences, although the minimum between the two maxima no longer reaches values below the initial level. At intermediate fluences, a shoulder develops at the temporal position of the minimum. For the 180 nm thick film, the transients do not present any more oscillations, but they do show a continuous decay at low fluences and a shoulder in the reflectivity decay in the high fluence range.

In all cases, the slow reflectivity rise observed (4–10 ns after the laser pulse) is related to the limited time resolution of the detection system used since, for the pulse duration used, the melting-induced reflectivity rise actually occurs within the pulse duration, as was shown in Ref. 31. For fluences just above the melt threshold (20 ± 5 mJ/cm^2 for all

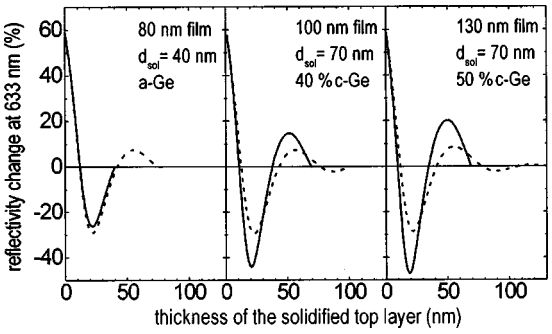

FIG. 2. Calculation of the reflectivity changes at 633 nm occurring in molten Ge films with different thicknesses on Si substrates upon surface initiated solidification. The dashed curves correspond to the case in which the solidification front reaches the substrate. The solid curves show the best fits in the solidification part of the transients in Fig. 1 obtained by adjusting the maximum depth d_{sol} that the solidification front reaches and the crystalline fraction of the solidified material, as indicated in the legends. The reflectivity changes were normalized to the reflectivity of the corresponding *a*-Ge film.

films), the transients recorded exhibit for all films a *continuous decay* after R_{max}. This behavior is consistent with an interfacial solidification process from a shallow initial melt depth towards the surface, as reported earlier for a 50 nm thick film.[30] This solidification scenario is favored because the large thermal gradient at the solid/liquid interface is caused by the fast heat flow towards the well conducting substrate. At high fluences, only the RTR transients of the thinner films (30 and 50 nm) maintain this shape, indicating an interfacial solidification process towards the surface.

The transients obtained at intermediate to high fluences in the thickest film (180 nm) and at intermediate fluences in the 130 nm thick film exhibit a *shoulder* instead of continuous decay. Similar transients have been observed earlier in Ge films on glass[11] and on Si (Ref. 32) upon ns laser pulse irradiation and in Ge films on glass upon ps laser pulse irradiation.[13] The appearance of the shoulder has been related to recalescence effects after a bulk solidification process, i.e., the release of latent heat upon solid phase nucleation leading to a temperature increase of the melt. Bulk solidification requires a melt at a homogeneous temperature in order to allow solid nuclei to form all over the molten volume. It has been found that recalescence occurs once a considerable melt depth (the amount of latent heat to be released is proportional to it) is induced *and* the melt solidifies via a bulk solidification process.[12,14,31,32] For films grown on thermally well conducting Si substrates, as in our case, these requirements are only met if the melt is not in direct contact with the substrate, i.e., they are thick films which are not entirely molten. In such a case, the remaining solid layer of *a*-Ge between the melt and the substrate acts as a thermal isolator due to its low thermal conductivity ($K_{a\text{-Ge}} = 0.01\,\mathrm{W/cm\,K}$), thus reducing the heat flow towards the substrate ($K_{c\text{-Si}} = 1.0\,\mathrm{W/cm\,K}$) and enabling homogenization of the temperature within the melt ($K_{l\text{-Ge}} = 0.3\,\mathrm{W/cm\,K}$).

The transients obtained at high fluences in the 80 and 100 nm thick films show an *oscillation-like* behavior that cannot be explained by either of the two solidification scenarios (interfacial or bulk solidification) discussed above. These oscillations are also observed in the 130 nm thick film for the highest fluences shown. Since similar oscillations have been observed upon explosive crystallization of amorphous films,[20,21] we have performed Raman spectroscopy measurements in the specimens after irradiation to determine if any crystalline material has formed. It is found that, although the 100 and 130 nm thick films contained crystalline material, the 80 nm thick film was amorphous over the whole fluence range studied. Thus, explosive crystallization has to be discarded as the responsible mechanism for the oscillations at least for the 80 nm thick film.

Oscillations below the initial reflectivity level like those observed in the 80 and 100 nm thick films can be consistent with the presence of interference effects in a system composed of a semitransparent solid layer on top of a reflecting liquid as would be the case upon surface initiated solidification. A more quantitative analysis of the RTR transients has thus been done by means of optical simulations to determine if the experimentally observed transients are consistent with the simulation of a surface initiated solidification process. The dashed curves in Fig. 2 show the evolution of the reflectivity at 633 nm taking place in completely molten Ge films upon re-amorphization through a surface initiated solidification process. Although the curves show oscillations similar to the ones observed experimentally (Fig. 1), the transient features are not strictly reproduced. For instance, no second maximum or second minimum is observed experimentally in the transients of the 80 and 130 nm thick films, respectively, as opposed to what is predicted by the simulations. To resolve this discrepancy, we have extended the simulations to consider that surface initiated solidification is accompanied by a counterpropagating front from the melt/solid interface towards the surface.[16] Furthermore, the crystalline fraction was also used as a fit parameter in the case of the 100 and 130 nm thick films for which Raman measurements revealed the presence of crystalline material upon solidification. The solid curves in Fig. 2 correspond to the best fits to the transients, taking into account these considerations. For the 80 nm thick film, the solidification depth d_{sol} at which both fronts meet is found to be 40 nm and no crystalline fraction was assumed since the film was found to be amorphous after solidification. For the 100 nm thick film, d_{sol} must definitively be larger than 40 nm since a second maximum is observed. A value of $d_{sol} = 70\,\mathrm{nm}$ and a crystalline fraction of 40% provide both the presence of a second maximum and $R_{max\,2}$ values similar to the ones observed experimentally (Fig. 1). For the 130 nm thick film, a similar value for d_{sol} is obtained and a crystalline fraction of 50% is suggested by the $R_{max\,2}$ values observed experimentally.

The fact that d_{sol} in the 100 and 130 nm thick films remains the same suggests that the thickness limit for surface initiated solidification is reached. In addition, since the simulations are capable of reproducing not only the results obtained for the 80 nm thick film, but also those for the 100 and 130 nm thick films, the results indicate that surface initiated solidification is *in all cases* the responsible mechanism when oscillations appear rather than explosive crystallization. The fact that the amplitude of the oscillation minimum (R_{min}) is much less pronounced in the experimental transients than in

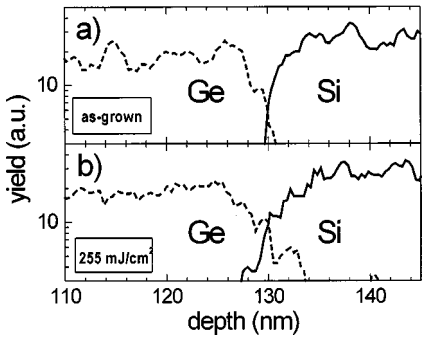

FIG. 3. Concentration profiles obtained by SIMS in a 130 nm film near the Ge/Si interface both for (a) an as-grown area of the Ge film on Si and (b) for an area that was exposed to a single laser pulse at 255 mJ/cm^2. The horizontal scale gives the actual depth of the specimen as calculated by the sputtering time.

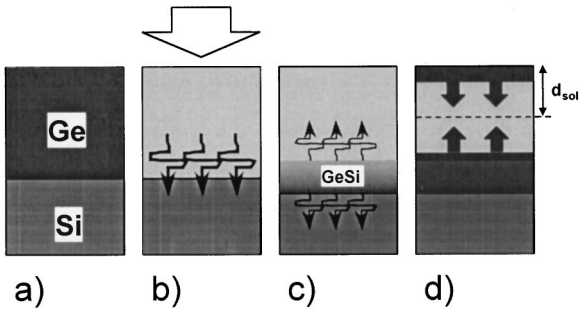

FIG. 4. Scenario of surface initiated solidification promoted by substrate melting at high fluences. (a) The solid *a*-Ge film on a Si substrate prior to irradiation. (b) Upon irradiation with a ps laser pulse the film melts over its entire depth and heat diffusion to the Si substrate occurs. (c) The surface of the Si substrate is melted and mixing is promoted at the interface with the liquid Ge. (d) The lower solidification temperature of the mixed layer promotes surface initiated solidification that is followed by solidification from the mixed layer towards the surface, d_{sol} being the depth at which both melt fronts meet.

the simulations is most likely due to the limited rise time of the detection system that becomes even more severe for large amplitude changes. A similar amplitude discrepancy was reported earlier when RTR transients with ns resolution were compared to those obtained with ps resolution using a streak camera.[22,23,31] It was reported that ns resolution measurements are not capable of following very fast reflectivity changes and lead to a reduction of the modulation amplitude of the transients. Even when the time resolution used in the present work is limited, it is still sufficient for our purpose here, i.e., to detect the presence of the minimum and therefore the occurrence of surface initiated solidification.

The comparison of the RTR transients with the optical simulations has shown that surface initiated solidification occurs in 80, 100, and 130 nm thick films in a given fluence interval.[33] Nevertheless, a solidification front initiated at the surface and propagating into the depth is apparently in conflict with the laws of thermodynamics, since the initial exponential temperature profile has its maximum at the surface. Such a surface initiated process can only be explained by inversion of the temperature gradient in the liquid that requires the *presence of a heat source underneath the surface*. Our hypothesis is that the laser pulse induces melting not only over the entire depth of the films but it also melts a very thin layer of the Si substrate. Upon solidification, this layer releases its corresponding latent heat partially towards the still liquid Ge, thus providing the required gradient inversion for surface initiated solidification. This hypothesis is further supported by the results for the 130 nm in which the oscillations are only observed for the largest fluences studied (and thus the deepest melt depths achieved) whereas for intermediate fluences a shoulder (related to recalescence and thus to melting of a thick layer but thinner than the film) is observed.

If a thin layer of the substrate at the film–substrate interface melts, significant diffusion of atoms is most likely to happen prior to solidification due to the extended solubility range of Si and Ge together with their high diffusivities in the liquid phase. As an example, the liquid phase diffusivity of Ge in Si and Ge_xSi_{1-x} is of the order of 10^{-4} cm^2/s,[8] which would lead to a diffusion length of $L_d=(4Dt)^{1/2}$ $\approx$6 nm within only 1 ns. To analyze if this diffusion process plays a role in the surface initiated solidification process, the concentration profiles of the resolidified films were studied by SIMS. Figure 3 shows the profiles obtained in the 130 nm thick film near the Ge/Si interface both for an as-grown area and for an area exposed to a single laser pulse at 255 mJ/cm^2. While the as-grown film shows a very sharp interface with minimal overlap between the concentration profiles of Si and Ge, the irradiated film clearly exhibits significant diffusion of Si and Ge (over a depth of $\approx$5 nm) at the interface.

IV. DISCUSSION

The results shown above provide evidence for the occurrence of a surface initiated solidification process in Ge films on Si under ps laser pulse irradiation. A few authors have already claimed the existence of an additional solidification scenario in Si beyond explosive crystallization, bulk solidification, and interfacial solidification towards the substrate.[15,16,19] Bruines *et al.*[16] irradiated 220 nm thick *a*-Si films on *c*-Si substrates with laser pulses of 7 ns. By means of RTR measurements with ns resolution they observed amorphous regrowth in both directions, from the surface towards the substrate and from the maximum melt depth towards the surface. These authors determined the initial melt depth in Cu-doped *a*-Si films by Rutherford backscattering spectrometry (RBS) by analyzing the impurity redistribution upon melting and subsequent solidification. They found that only when the whole film thickness was molten, reamorphization from the surface was prevented and single-crystal epitaxial regrowth from the substrate did occur. As an explanation for surface initiated solidification they suggested that heat extraction at the solid–liquid interface after melt-in was so efficient that the temperature of the surface rapidly decreased to the solidification temperature and that solid nuclei formed at impurities. But, this explanation is not entirely satisfactory because it does not explain why they did not observe surface initiated solidification for completely molten films despite the fact that heat extraction by *c*-Si is much more efficient than that by a system with a buffer layer of nonmolten *a*-Si.

In our case of Ge films, substrate melting has experimentally been identified as being related to the occurrence of surface initiated solidification (Fig. 3). In spite of the large thermal diffusivity of the substrate, thin Ge films on Si are likely to melt completely at high fluences. Notice that the fluences used here are higher than those at which films on glass have been shown to melt completely[13] although they show a lower optical absorption at 583 nm. For a completely molten film, direct contact with the very hot molten Ge causes the Si substrate to be heated substantially and even melted. It is worth noting that melting of the substrate is only likely to happen because the amorphous Ge film serves as an ''absorption layer'' ($1/\alpha = 23$ nm) which transmits the heat to the Si. Direct irradiation of the bare Si substrate at the same fluence would not necessarily lead to melting due to the much larger optical penetration depth of Si at 583 nm ($1/\alpha = 1720$ nm).

The complete process leading to the surface initiated solidification scenario consistent with the present results is schematically drawn in Fig. 4. At high fluences, the Ge film is melted over its entire depth [Fig. 4(b)] within a time comparable to the pulse duration.[13,31] Large thermal gradients within the very hot liquid (melting point = 937 °C, boiling point = 2830 °C) are initially present and rapidly thermalize at the mean time heat diffuses to the Si substrate. The latter causes a thin Si layer to melt (melting point = 1412 °C) slightly after the whole film is melted [Fig. 4(b)]. The large thermal conductivity of liquid Ge ($K_{l\text{-Ge}} = 0.3$ W/K cm) enables a continuous supply of heat in order to provide the melt enthalpy of Si. This process leads, after a few hundreds of ps, to a situation in which both liquids have similar temperatures and start to mix. As a consequence of this diffusion process in the liquid phase at rates higher than 10^{-4} cm^2/s,[8] a mixed layer with a solidification temperature varying continuously between that of the solid Si and Ge is formed [Fig. 4(c)]. The high concentration gradient involves a large constitutional undercooling which promotes further lowering of the solidification temperature of the mixture to values well below those of the single element components[34] and thus delays the solidification process at the substrate–film interface [Fig. 4(d)]. The depressed temperature of the mixed layer and the fast release of its latent heat to the well conducting Si substrate and liquid Ge inverts the temperature gradient within the liquid Ge film and thus facilitates solidification to be initiated at the surface while the inner part of the film and the mixed interface are still liquid.

When comparing the present results to those of other authors using ns laser pulses, it is essential to note that the pulse duration plays an essential role in the occurrence of surface initiated solidification. Using 7 and 20 ns laser pulses, re-amorphization from the surface[16] and explosive crystallization[35] in the *same sample type* (200 nm thick *a*-Si film on *c*-Si), respectively, have been reported. The influence of the pulse duration on the solidification scenario is further confirmed by the fact that the few times surface initiated re-amorphization has been reported, the pulse duration used has always been of few ns (Refs. 15–19) or even less, as it is in our case (30 ps). For such short pulses, complete melting of the film and the substrate can be induced within a extremely short time, thus allowing the fast inversion of the thermal gradient to occur in a time at which the supply of energy to the surface is already finished. Such a scenario is not possible with laser pulses of tens of ns because the relatively long tail of such a pulse supplies continuous energy to the surface at times when the whole film (and eventually a thin substrate layer) is already melted, thus preventing solidification to take place at the surface.

Bruines *et al.*[36] have also studied by means of cross-sectional transmission electron microscopy those samples that showed surface initiated solidification after irradiation. They found that the irradiated areas presented a laterally random pattern of amorphous material and polycrystalline Si (*p*-Si) embedded in an amorphous matrix. They concluded that amorphous regrowth occurred from both the surface and the substrate and that *p*-Si must have been nucleated at the *l*-Si/*a*-Si interface during the last stages of the solidification processes. Our observation of both amorphization and crystallization upon surface initiated solidification depending on the film thickness is perfectly consistent with their observation. Since we have determined the approximate maximum solidification depth d_{sol} for the 80, 100, and 130 nm thick films by comparing the experimental results in Fig. 1 to the calculated results shown in Fig. 2, we can determine the approximate velocity v_{surf} of the surface initiated solidification front by dividing d_{sol} by the time the transients take to recover the initial reflectivity level. This leads to approximate values of $v_{\text{surf}}(80\text{ nm film}) = 1.4$ m/s, $v_{\text{surf}}(100\text{ nm film}) = 1.7$ m/s, and $v_{\text{surf}}(130\text{ nm film}) = 1.5$ m/s, which suggests that the velocity of the surface initiated solidification front can be considered reasonably constant. In spite of the relatively large error of these values due to the limited time resolution of our detection system, the value estimated for the 80 nm thick film is in reasonable agreement with the values measured with a streak camera in Ge films on a glass substrate, in which interfacial amorphization towards the surface is observed to occur at velocities as low as 1.7 m/s.[31] The result also implies that the solidification velocity alone cannot be responsible for the fact that the 80 nm thick film amorphizes whereas the 100 and 130 nm thick films partially crystallize. It is, rather, the film thickness and therefore the amount of initially melted material that determine the final phase of the material after solidification. For thicker films and thus larger melt depths, a higher amount of total heat is deposited that can induce partial crystallization of the film even after its initial amorphization. This interpretation is consistent with the fact that the decrease of reflectivity to the value corresponding to the crystalline material (5%–10% below the initial reflectivity level of the amorphous film, not shown in Fig. 1) occurs at a time (>45 ns) at which the solidification process has already terminated.

A direct comparison of our results to others obtained also in Ge with a longer pulse duration [full width at half maximum (FWHM) = 12 ns, $\lambda = 193$ nm], and even in *the same samples* we study in this work, can be done using Ref. 32. These authors did not observe surface initiated solidification (oscillatory RTR transients) but bulk solidification accompanied by recalescence (RTR transients containing a shoulder). By means of heat flow calculations and measure-

ments of the threshold fluences to observe recalsecence effects in all the film thicknesses studied, it was shown that recalescence (and also bulk solidification) requires a minimum melt depth. Their result is consistent with the fact that the fluences at which we observe bulk solidification (in the 130 and 180 nm thick films) upon ps laser pulses are considerably above the melt threshold which suggests that also for ps pulses a minimum melt depth for the occurrence of bulk solidification is required. The fact that for thinner films we do not observe recalescence through a bulk solidification process but interfacial solidification towards the substrate (low fluences) and surface initiated solidification (high fluences) can thus be solely attributed to the use of ps pulses. Such short pulses generate a strong thermal gradient within the partially molten film at low fluences whereas they may lead to substrate melting at high fluences and therefore to surface initiated solidification. In contrast, the much longer pulses used by Vega *et al.*[32] prevent this solidification scenario due to their long lasting supply of heat to the surface and for the same reason they tend to favor processes like recalescence and bulk solidification.

V. CONCLUSION

We have reported a surface initiated solidification process that takes place in amorphous Ge films (80–130 nm) on Si substrates under ps pulsed laser irradiation in the high fluence regime. This process leads either to complete reamorphization (80 nm thick film) or to some degree of recrystallization (100 and 130 nm thick films). The occurrence of such a process is accompanied by melting of a thin layer of the Si substrate and interdiffusion of Ge and Si. The heat released upon solidification of this mixture together with its lower solidification temperature due to constitutional undercooling invert the temperature gradient and promote solidification at the film surface while the mixed layer at the film–substrate interface is still liquid. The delayed solidification of the mixed layer produces a delayed solidification front propagating towards the surface. A transition from a surface initiated solidification process towards a bulk solidification process occurs at a film thickness of 130 nm at intermediate fluences, while for even thicker films (180 nm) bulk solidification is the dominant process. This suggests that significant melting of the substrate cannot be obtained for thicker films and confirms that a bulk solidification process requires the suppression of rapid heat extraction towards the substrate. This reduced heat extraction is achieved in our case by the influence of the nonmolten amorphous Ge layer remaining between the liquid film and the Si substrate which acts as a ''thermal insulator.'' Finally, besides film thickness, the pulse duration has a major influence on the type of solidification scenario induced. In particular, it can be concluded that only pulses of a few ns or shorter are capable of triggering a surface initiated solidification process whereas longer pulses favor processes such as recalescence and bulk solidification.

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rence of surface initiated solidification at high fluences (Refs. 22 and 23). The ns temporal resolution of the technique used in the present work is not sufficient to resolve the ultrafast reflectivity oscillations occurring in a 50 nm thick film whereas they can easily be resolved for thicker films, as seen in Fig. 1.

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